



TREATMENT OF 1,2-DIBROMO-3-CHLOROPROPANE AND NITRATE-CONTAMINATED WATER WITH ZERO-VALENT IRON OR HYDROGEN/PALLADIUM CATALYSTS

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Abstract—The abilities of zero-valent iron powder and hydrogen with a palladium catalyst (H₂/Pd-alumina) to hydrodehalogenate 1,2-dibromo-3-chloropropane (DBCP) to propane under water treatment conditions (ambient temperature and circumneutral pH) were compared. DBCP reacted with iron powder (100–200 mesh, 36 g/l) in HEPES-buffered water (pH = 7.0) with a *t*_{1/2} of 2.5 min and in different groundwaters (pH = 8.2–8.7) with a *t*_{1/2} ranging from 41–77 min. Dissolved O₂ and NO₃[−] slowed the transformation, whereas sulfate and nitrite had little effect. Iron removed 60 mg/l of nitrate within 14 min with nitrite as an intermediate. In 75 ml groundwater containing 22.5 mg 1% Pd-alumina catalyst under 10% H₂ partial pressure, DBCP was transformed to propane within minutes. The rate in groundwater was slower by about 30% compared to Milli-Q[™] water. SO₄^{2−}, NO₃[−], Cl[−] or O₂ added to Milli-Q water only slightly inhibited DBCP transformation by H₂/Pd-alumina, while SO₃^{2−} had a much stronger inhibitory affect. Copyright © 1996 Elsevier Science Ltd

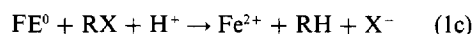
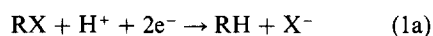
Key words—chlorinated hydrocarbons, DBCP (1,2-dibromo-3-chloropropane), nitrate, oxygen, hydrogen, iron metal, palladium catalyst, hydrodechlorination, dechlorination, reduction

INTRODUCTION

Although the soil nematicide, 1,2-dibromo-3-chloropropane was banned in 1977, it still contaminates groundwater in California (Schmidt and Sherman, 1987) and elsewhere above the maximum contaminant limit (MCL) of 0.2 µg/l. Methods are needed to effectively remove DBCP from groundwaters used as water supplies. Conventional treatment methods of halogenated aliphatics include air stripping or granular activated carbon contacting. However, these processes produce secondary waste streams that must be treated at an additional expense. Processes that transform the contaminants to non-hazardous products are potentially more economical than processes which simply move the contaminants from one medium to another.

Destruction of halogenated hydrocarbons (RX) using zero-valent metals such as iron (Fe⁰) (Sweeney and Fisher, 1972; Sweeney, 1981; Senzaki and Kumagai, 1988, 1989, 1991; Gillham, 1993; Matheson and Tratnyek, 1994; Schreier and Reinhard, 1994) and catalytic hydrodehalogenation

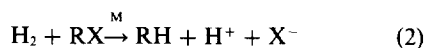
employing Pd and other catalysts (Rylander, 1979; Balco *et al.*, 1993; Kovenklioglu *et al.*, 1993; Miyabe *et al.*, 1993; Schreier and Reinhard, 1995; and others) are technologies currently being studied for either *in situ* or above-ground treatment of groundwater. Fe⁰ is a mild reductant which may reductively dehalogenate RX according to equations (1). The half reaction in equation (1a) is thermodynamically favorable for several brominated and chlorinated methanes, ethanes and ethylenes under water treatment conditions (pH 7, 25°C, Cl[−] activity = 0.001, Br[−] activity = 0.00001) (Vogel *et al.*, 1987). Because these compounds are structurally similar to DBCP, reductive dehalogenation of DBCP is also expected to be favorable. Since the oxidation of Fe⁰ to Fe²⁺, equation (1b), is thermodynamically favorable (Weast, 1983–1984), the reduction of DBCP by Fe⁰, equation (1c), should also be favorable.



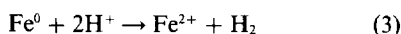
Hydrogen gas is usually inert, but in the presence of a suitable metal catalyst (M) such as Pd, Ni, Pt

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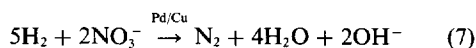
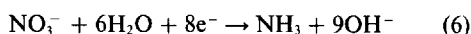
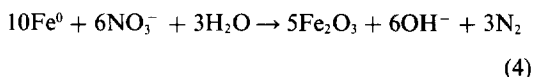
(Rylander, 1979) or possibly Fe^0 , hydrodehalogenation of RX is facile:



Note that this reaction is analogous to equation (1c) except that H_2 rather than Fe^0 is the reducing agent. Because under anaerobic conditions Fe^0 can react with protons to form H_2 , equation (3), (Evans, 1981), Fe^0 may potentially function both as a reactant, equation (1c), and as a catalyst, equation (2), during DBCP destruction. For Pd and other non-water reactive metal catalysts, an external hydrogen source such as H_2 , hydrazine, BH_3 or iron metal must be used.



In addition to RX, ground and surface waters often contain electron acceptors such as oxygen, nitrate, nitrite, and sulfate, which could potentially interfere with the hydrogenolysis of RX. For example, in some areas, high DBCP levels coincide with high nitrate levels (Schmidt and Sherman, 1987) so the behavior of nitrate during DBCP destruction is of particular interest. Siantar *et al.* (1995) reported that Fe^0 may also be useful for treating nitrate and nitrite-contaminated water since these compounds disappeared in the presence of the metal. In addition, Flis (1991) reported that iron may reduce nitrate to nitrogen, equation (4), nitrite, equation (5), or ammonia, equation (6), depending upon the reaction conditions. (Note that the iron reaction was not given in equation (6), presumably because the identity of the oxidized form is uncertain.) Nitrate can also be reduced to nitrogen using H_2 and Pd-on-copper, equation (7), under water treatment conditions (Sell *et al.*, 1993).



The reactivity of Fe^0 with RX depends on substrate structure among other factors. Fe^0 was found to transform tetrachloroethylene and trichloroethylene rapidly to ethene, ethane and unidentified products, but dichloromethane and 1,1-dichloroethane were relatively nonreactive (Gillham and O'Hannesin, 1994; Schreier and Reinhard, 1994). Chlorinated ethylenes were rapidly dechlorinated in tap water with H_2 and Pd-on-carbon without the formation of significant amounts of intermediates (Schreier and Reinhard, 1995). Muftikian *et al.* (1995) reported facile hydrodechlorination of chlorinated ethylenes to ethane and relatively slower reaction of polychloromethanes to methane using palladized iron.

DBCP hydrodehalogenation by Fe^0 and H_2/Pd catalysts has not been studied. Based on literature

data, the reaction scheme in Scheme 1 can be proposed. The upper pathway is a sequence of three hydrodehalogenation reactions, each requiring a proton and two electrons. The lower pathway indicates the transient formation of propene followed by hydrogenation of the double bond to form propane. Since a number of different initial reactions including elimination and hydrodehalogenation reactions are possible, the observed DBCP transformation rate constant, k_{obs} , is the summation of all initial reactions. For reactions at nonporous solid surfaces (e.g., Fe^0 powder), the rates follow pseudo-first-order kinetics;

$$-\frac{d[\text{DBCP}]_{\text{aq}}}{dt} = k_{\text{obs}}^1 [\text{DBCP}]_{\text{aq}} \quad (8)$$

For reactions in porous supports (e.g., Pd/ γ - Al_2O_3 pellets), the rates may be mass transfer limited and the initial reaction is zero-order:

$$-\frac{d[\text{DBCP}]_{\text{aq}}}{dt} = k_{\text{obs}}^0 \quad (9)$$

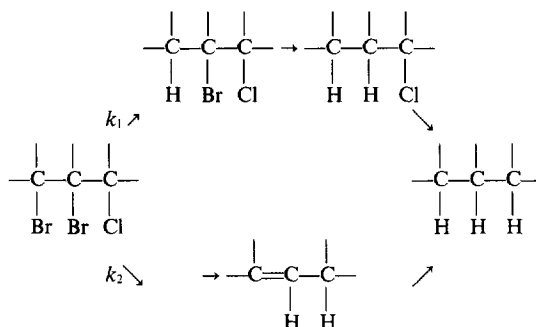
k_{obs}^1 and k_{obs}^0 are the observed first- and zero-order rate constants, respectively.

In this study, we compare the ability of Fe^0 and H_2/Pd to reductively dehalogenate DBCP at room temperature ($22^\circ\text{C} \pm 1^\circ\text{C}$) in aqueous solution. Both sterile, abiotic, Milli-Q[™] water and non-sterile groundwater were studied. The objectives of this work were to (i) develop rate data for DBCP hydrodehalogenation by Fe^0 and H_2/Pd , (ii) investigate the effect of water quality on the DBCP transformation rate, and (iii) study the NO_3^- reduction by Fe^0 .

EXPERIMENTAL

Materials and reagents

DBCP and Fe^0 were obtained from Pfaltz & Bauer and Alfa AESAR, respectively. DBCP was used as received without further purification. Fe^0 powder was sieved into three different iron size fractions, <48–100, 100–200, and >200 mesh, and was stored in a glove box under approximately 0.1 atm H_2 partial pressure for at least 2 weeks before use. The BET specific surface areas of different Fe^0 size fractions were not measured. Zero-grade N_2 and O_2 gases were from Liquid Carbonic. HEPES (*N*-[2-hydroxyethyl]piperazine-*N'*-[2-ethanesulfonic acid]) was from Sigma and used as received. The activated carbon was



Scheme 1

CECA Carbon B; 8×30 mesh from Carborundum[™]. Various acids and sodium salts were obtained from Baker.

The 0.5% Pd-on- γ -alumina (γ -Al₂O₃) pellets (3.2–3.4 mm) were obtained from Aldrich. The 1% Pd/ γ -Al₂O₃ powder ($\sim 32 \mu\text{m}$) or (20–120 μm) was either from Aldrich or Alfa AESAR. The 1% Pd-on-activated carbon (C) powder (~ 325 mesh) was from Aldrich. The 1% Pd-on-polyethylenimine (PEI)/Silica (SiO₂) powder (40–200 mesh) and PEI/SiO₂ beads (20–40 mesh) were both from GFS. All the Pd catalysts were pre-reduced by vacuum drying at 120°C and stored overnight in a ~ 0.1 atm/H₂ glove box.

Analytical methods

Reactions of Fe⁰, DBCP, and nitrate. Experiments were conducted in a glove box containing a reducing atmosphere (approximately 90% N₂/10% H₂). In a typical experiment, a 125 ml glass serum bottle was filled with 4 g of 100–200 mesh iron powder and 110 ml of aqueous solution which had been deoxygenated (by purging with zero-grade N₂ gas), autoclaved, and spiked with DBCP to give about 40 nM (10 $\mu\text{g/l}$) solution. The bottle closure was a crimp-style Mininert[™] valve. The aqueous phase was either Milli-Q[™] (deionized) water or non-sterile groundwater which in some cases had been amended with various anions and/or HEPES buffer at pH = 7.0. Neutral pH was chosen since our preliminary studies with organic buffers indicated that at or above pH 9.0, DBCP was not transformed. Control experiments containing no Fe⁰ powder were also prepared. DBCP removal was followed by extracting 1.5 ml aliquots with 0.5 ml pentane then analyzing the pentane using a Hewlett-Packard (HP) Series II 5890 gas chromatograph (GC) equipped with an electron capture detector (GC/ECD) and a 30 m DB-1 fused silica capillary column (1.5 micron film thickness; J & W Scientific). Analyses were isothermal at 120°C. Propane and propene were measured by analyzing headspace on a HP 5730A gas chromatograph equipped with a flame ionization detector (GC/FID) and Carbosieve G column (Supelco). Most experiments were done in duplicate. All experimental errors are reported as 95% confidence intervals. The reactions were conducted outside the glove box at room temperature ($22^\circ\text{C} \pm 1^\circ\text{C}$) with 400 rpm orbital shaking. A Dionex 4000i Ion Chromatograph served to measure bromide (Br⁻), chloride (Cl⁻), nitrite (NO₂⁻), nitrate (NO₃⁻), and sulfate (SO₄²⁻). The procedures were the same as for DBCP transformation, except that NO₃⁻ rather than DBCP was the substrate.

Reactions with Fe⁰ in groundwater. A series of tests were conducted to compare DBCP transformation by Fe⁰ in Milli-Q[™] water and in groundwater. The pH in groundwater was adjusted to 7 either with 0.1 M HEPES buffer or one of the following acids: HClO₄, H₂SO₄, HCl, HNO₃, or CH₃COOH. The pH in the activated carbon pretreated groundwater was adjusted with acetic acid.

Groundwater was obtained from the Central Valley, California and analyzed in early September 1994. General minerals analyses indicated: 5 mg/l Cl⁻, 16 mg/l SO₄²⁻, 25 mg/l NO₃⁻, 138 mg/l HCO₃⁻, 3 mg/l K⁺, 15 mg/l Mg²⁺, 16 mg/l Na⁺, 30 mg/l Ca²⁺, 235 mg/l total dissolved solids and 338 $\mu\text{S/cm}$ conductance. Groundwater from the same site was used in both the Fe⁰ and Pd experiments.

Reactions of H₂/Pd and DBCP. Experiments were prepared and conducted as for Fe⁰, but used Pd catalyst instead of Fe⁰. The performance of various Pd catalysts was compared by conducting kinetic experiments with the following supports: γ -Al₂O₃ pellets, γ -Al₂O₃ powder, activated C powder, PEI/SiO₂ powder or PEI/SiO₂ beads. In all cases, Pd loading was 1% and 22.5 mg catalyst was added to 75 ml of Milli-Q[™] water (or 3 mg/l Pd content) and spiked with DBCP to give 22 μM solution. Similar experiments using powdered γ -Al₂O₃, C and beaded PEI/SiO₂ but with tetrachloroethylene (PCE) as substrate were also conducted.

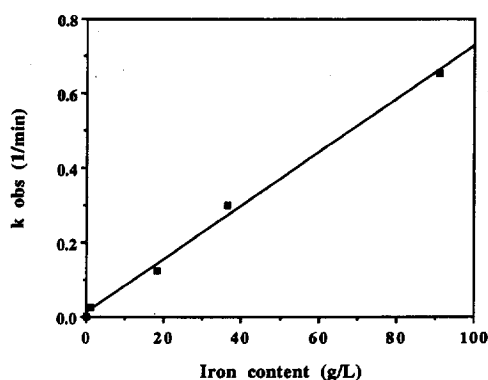


Fig. 1. Effect of zero-valent iron content on the observed pseudo-first-order rate constant of DBCP transformation using 0–90.9 g/l Fe⁰ powder (100–200 mesh) in 0.1 M HEPES-buffered Milli-Q[™] water (pH 7.0) spiked with 40 nM DBCP at 22°C and 0.1 atm H₂ partial pressure.

The reactions of H₂/Pd in groundwater were studied by adding one to four pellets (45–180 mg) of 0.5% Pd/ γ -Al₂O₃ to 75 ml of non-sterile groundwater and spiked with DBCP to give approximately 20 μM solution.

RESULTS AND DISCUSSION

Reactions with Fe⁰ in HEPES buffer at pH 7.0

Effect of Fe⁰ content and particle size. Preliminary experiments indicated that Fe⁰ was inactive unless it was first stored in the anaerobic glove box. The mechanism of iron activation is not clear but was probably due to the displacement of physi- and chemisorbed oxygen by either N₂ or H₂ (O₂ oxidizes iron in aqueous solution, which could interfere with the Fe⁰/DBCP reaction) or to hydrogen spillover on the metal surface (Conner, 1988). Further work is required to determine the cause of activation and to ascertain the role—if any—of H₂.

The transformation of DBCP by Fe⁰ (36.4 g/l) in HEPES-buffered Milli-Q[™] water was pseudo-first-order with respect to DBCP, with a $t_{1/2}$ of 2.5 ± 0.3 min ($k_{\text{obs}} = 0.28 \pm 0.03 \text{ min}^{-1}$). The disappearance rate was about four times faster in this system than in unbuffered Milli-Q[™] water. The final product was propane with propene as an intermediate. Complete dehalogenation was confirmed by the removal of two Br⁻ and one Cl⁻ per DBCP molecule transformed (data not shown).

Figure 1 shows a first-order dependence of DBCP transformation of Fe⁰, presumably because the reactive Fe⁰ site concentration increases proportionally with the Fe⁰ concentration. The linear regression of k_{obs} versus Fe⁰ content was:

$$k_{\text{obs}}^1 (\text{min}^{-1}) = (0.007 \pm 0.001)[\text{Fe}^0 \text{ content (g/l)}] + 0.011 \text{ where } r^2 = 0.996 \quad (10)$$

Increasing the surface area by using a constant amount of Fe⁰ (36.4 g/l) but smaller size fractions also increased the rate of DBCP transformation (Table 1). Because the average surface areas of the size fractions

Table 1. Effect of iron size fractions on the pseudo-first-order rate constants of DBCP transformation using 36.4 g/l Fe⁰ powder of different mesh in 0.1 M HEPES-buffered Milli-Q[™] water (pH 7.0) spiked with 40 nM DBCP at 22°C and 0.1 atm H₂ partial pressure

Iron size fractions	$k_{\text{obs}}^1 (\text{min}^{-1})^a$
< 48–100 mesh	0.22 ± 0.03
100–200 mesh	0.28 ± 0.03
< 200 mesh	0.39 ± 0.07

^aErrors are at 95% confidence intervals.

were not measured, the rate law cannot be expressed in terms of surface area concentration.

Effect of water quality. The effects of some reducible species including dissolved oxygen, SO₄²⁻, and NO₃⁻ were examined; these may occur in water and may potentially compete with or inhibit the reduction of DBCP. Increasing the amount of dissolved O₂ from 0 to 41.6 mg/l (saturation concentration of O₂ in water at 22°C) decreased k_{obs}^1 linearly from 0.28 ± 0.03 to $0.07 \pm 0.02 \text{ min}^{-1}$ (Fig. 2). The linear regression of k_{obs}^1 versus dissolved O₂ was:

$$k_{\text{obs}}^1 (\text{min}^{-1}) = (0.0049 \pm 0.0001)[\text{O}_2 (\text{mg/l})] + 0.278 \text{ where } r^2 = 0.983 \quad (11)$$

This observation may indicate that DBCP competes with O₂ for iron surface active sites and/or the O₂ deactivates the surface by forming nonreactive iron oxide coatings. (A reddish-brown precipitate—presumably hydrous iron (III) oxide or rust—was observed in solutions with higher dissolved O₂.) The inhibitory effect in typical surface or groundwater would be expected to be small, however. In the O₂ concentration range relevant for groundwater (0–10 mg/l), the DBCP transformation rate is expected to be lowered only by a maximum of 17%.

Increasing the SO₄²⁻ concentration had no effect on the transformation rate (Table 2). Neither the SO₄²⁻ nor the phosphate (a minor contaminant in the Na₂SO₄ used concentrations changed over the course

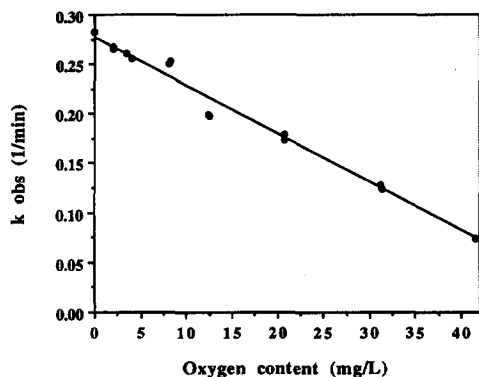


Fig. 2. Effect of dissolved oxygen on the observed pseudo-first-order rate constant of DBCP transformation using 0–41.6 mg/l O₂ and 36.36 g/l Fe⁰ powder (100–200 mesh) in 0.1 M HEPES-buffered Milli-Q[™] water (pH 7.0) spiked with 40 nM DBCP at 22°C and 0.1 atm H₂ partial pressure.

Table 2. Effect of dissolved sulfate and nitrite ions on the pseudo-first-order rate constants of DBCP transformation using 36.4 g/l Fe⁰ powder (100–200 mesh) in 0.1 M HEPES-buffered Milli-Q[™] water (pH 7.0) spiked with 40 nM DBCP at 22°C and 0.1 atm H₂ partial pressure (see Fig. 3 for the effect of dissolved nitrate)

System	$k_{\text{obs}}^1 (\text{min}^{-1})^a$
No ions added	0.28 ± 0.03
SO ₄ ²⁻ (mg/l)	
3.7	0.27 ± 0.05
19.8	0.27 ± 0.03
27.6	0.27 ± 0.02
NO ₂ ⁻ (mg/l)	
4.3	0.26 ± 0.01

^aErrors are at 95% confidence intervals.

of reaction, indicating that neither anion was reduced by iron (data not shown).

In contrast, NO₃⁻ was 90% removed within approximately 5 min, yet removal of DBCP did not begin for an additional 1–3 min (Fig. 3). This implies that intermediates such as NO₂⁻ or other partially reduced species may also compete with DBCP, thereby inhibiting the DBCP transformation. This is supported by the observation that 4.3 mg/l NO₂⁻ delayed the onset of DBCP transformation

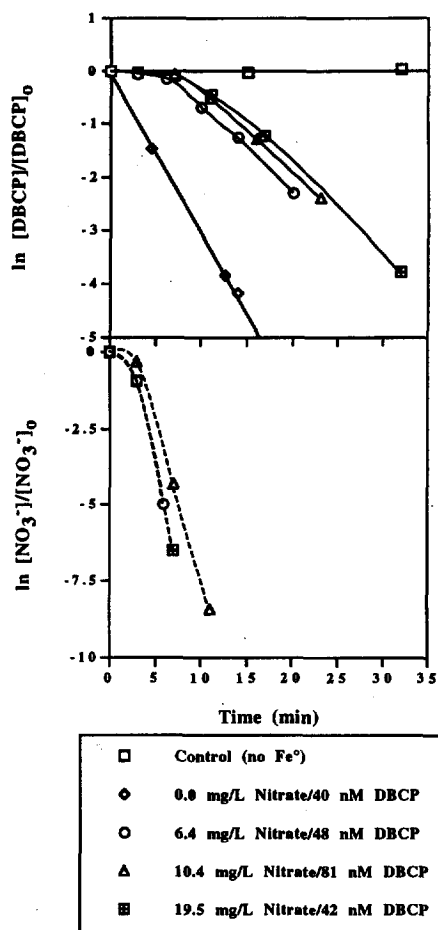


Fig. 3. Comparison of DBCP and nitrate transformation using 36.4 g/l Fe⁰ powder (100–200 mesh) in 0.1 M HEPES-buffered Milli-Q[™] water (pH 7.0) at 22°C and 0.1 atm H₂ partial pressure.

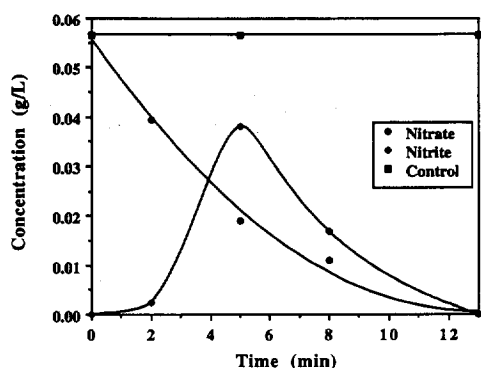


Fig. 4. Pseudo-first-order reduction of nitrate by 36.4 g/l Fe^0 powder (100–200 mesh) in 0.1 M HEPES-buffered Milli-Q[™] water (pH 7.0) spiked with 56.6 mg/l nitrate at 22°C and 0.1 atm H_2 partial pressure showing the removal of nitrate via the nitrite intermediate which was also completely reduced by iron. Lines on the control and NO_3^- data were fitted, while the line on the NO_2^- data is an arbitrary polynomial fit (NO_2^- data did not fit a simple kinetic model).

(data not shown) as well as decreased the rate of reaction (Table 2).

Reduction of nitrate and nitrite by iron. Under anaerobic conditions, nitrate (0.0566 g/l) was reduced by 100–200 mesh Fe^0 (36.4 g/l) within 14 min with nitrite as an intermediate (Fig. 4). The reaction was pseudo-first-order in nitrate with a k_{obs}^1 of $0.208 \pm 0.04 \text{ min}^{-1}$ ($t_{1/2} = 3.3 \pm 0.7 \text{ min}$).

Nitrate removal by Fe^0 was studied in a series of kinetic experiments containing the following initial NO_3^- concentrations: 0.0566 g/l, 0.51 g/l, and 2.73 g/l. Although NO_3^- was completely removed within 14 min if the initial concentration was low (56.6 mg/l), only about 5% was transformed in the same amount of time if the initial concentration was 2.73 g/l (data not shown). The mechanisms for this apparent inhibition or competition are not clear. Perhaps, partially reduced intermediates compete with NO_3^- for reactive sites. At the lower NO_3^- concentration tested (0.51 g/l), the apparent inhibitory effect was also evident although to a lesser degree (76% of the NO_3^- was removed after 16 min). During nitrate reduction, nitrite was also completely removed by iron.

Transformation of DBCP in groundwater. DBCP transformation in unbuffered groundwater obtained from three different wells (designated #1–3) was about 16–31 times slower than in HEPES-buffered Milli-Q[™] water (pH 7.0). Half-lives ranged from $41 \pm 7 \text{ min}$ to $77 \pm 9 \text{ min}$ (Table 3). The higher pH in the groundwater samples was considered a possible reason for the slower transformation rate—the initial pH values of 8.2–8.7 increased to about 9 over the course of the reaction. Adjusting the pH of the groundwater to 7.0 with HClO_4 , H_2SO_4 , or acetic acid increased the transformation rates by about 25% compared to unamended groundwater, while buffering it with HEPES (pH 7.0) increased the rate about

seven-fold (Table 3). This difference may be due to buffer effects of HEPES—specifically, Lipczynska-Kochany *et al.* (1994) hypothesized that the sulfonic acid group in HEPES was responsible for enhanced dechlorination of carbon tetrachloride by Fe^0 . If the pH was adjusted with HCl and HNO_3 rather than one of the acids listed above, then the transformation rate decreased by 50%. The decrease in rate was presumably due to competition between NO_3^- and Cl^- and DBCP, since our results above indicate that NO_3^- competed with DBCP in HEPES-buffered Milli-Q[™] water and since Cl^- could form transient compounds such as $3\text{Fe}(\text{OH})_2 \cdot \text{Fe}(\text{OH})_2\text{Cl} \cdot n\text{H}_2\text{O}$ ($3 \geq n \geq 2$) or “green rust 1” (Bernal *et al.*, 1959) which could potentially influence the rate of DBCP transformation.

Although the addition of HEPES buffer to groundwater increased the rate of DBCP transformation, the rate ($t_{1/2} = 5.8 \pm 0.5 \text{ min}$) was still slower than in HEPES-buffered Milli-Q[™] water ($t_{1/2} = 2.5 \pm 0.3 \text{ min}$). This suggests that factors other than pH may affect the rate. (Recall that although NO_3^- caused a delay in the onset of DBCP transformation, it did not significantly affect the rate of transformation.) To test whether dissolved organic matter in the groundwater composition had a detrimental effect, the groundwater was treated with activated carbon before conducting the experiment. No improvement in reaction rate was observed (see Table 3). The presence of bicarbonate (138 mg/l) in groundwater could hinder DBCP transformation due to precipitation of FeCO_3 onto the iron surface, but this possibility was not investigated. (Typically, the pH at the end of an experiment was between 7.2 and 7.6 implying that some Fe^{2+} was indeed formed via equation (1) and/or (3).)

Reactions with H_2 and palladium catalysts

Performance of various catalysts in Milli-Q[™] water. DBCP transformation using powdered ($\gamma\text{-Al}_2\text{O}_3$, PEI/ SiO_2 or activated C) and beaded (PEI/ SiO_2) catalyst supports resulted in pseudo-first-order

Table 3. The half-lives of DBCP transformation using 36.4 g/l Fe^0 powder (100–200 mesh) in groundwater (spiked with 40 nM DBCP at 22°C and 0.1 atm H_2 partial pressure) before and after pH adjustment of the groundwater by adding appropriate amounts of CH_3COOH , HClO_4 , H_2SO_4 , HCl , HNO_3 acid, or HEPES buffer

Water source	Compound added	pH (before)	$k_{\text{obs}}^1 (\text{min}^{-1})^a$ (before)	pH (after)	$k_{\text{obs}}^1 (\text{min}^{-1})^a$ (after)
Well #1	HClO_4	8.2	0.009 ± 0.001	7.0	0.013 ± 0.002
Well #3	H_2SO_4	8.7	0.011 ± 0.002	7.0	0.014 ± 0.001
Well #3	CH_3COOH	8.7	0.011 ± 0.002	7.0	0.013 ± 0.001
Well #3 (carbon filtered)	CH_3COOH	8.7	0.011 ± 0.002	7.0	0.014 ± 0.004
Well #2	HCl	8.3	0.017 ± 0.003	7.0	0.009 ± 0.001
Well #3	HCl	8.7	0.011 ± 0.002	7.0	0.006 ± 0.001
Well #1	HNO_3	8.2	0.009 ± 0.001	7.0	0.004 ± 0.001
Well #2	HEPES	8.3	0.017 ± 0.003	7.0	0.12 ± 0.01
Milli-Q	HEPES	— ^b	0.07	7.0	0.28 ± 0.03

^aErrors are 95% confidence intervals.

^bpH not measured. Estimated pH \approx 6.

Table 4. Effect of catalyst supports on the rate constants of DBCP transformation and PCE transformation normalized to 1 mg/l Pd content in unbuffered Milli-Q[™] water spiked with 22 μ M DBCP and 18 μ M PCE, respectively, at 22°C and 0.1 atm H₂ partial pressure. PCE transformation rate by Pd/C was obtained from Schreier and Reinhard (1995)

Catalyst support	DBCP experiment k_{obs}^a	PCE experiment k_{obs}^a
γ -Al ₂ O ₃ pellets	$0.50 \pm 0.07 \mu\text{M}/\text{min}$	
γ -Al ₂ O ₃ powder	$0.07 \pm 0.01 \text{ min}^{-1}$	$0.08 \pm 0.01 \text{ min}^{-1}$
PEI/SiO ₂ powder	$0.020 \pm 0.002 \text{ min}^{-1}$	
Activated C powder	$0.008 \pm 0.001 \text{ min}^{-1}$	$0.008 \pm 0.003 \text{ min}^{-1}$
PEI/SiO ₂ beads	$0.007 \pm 0.001 \text{ min}^{-1}$	$0.007 \pm 0.003 \text{ min}^{-1}$

^aErrors are 95% confidence intervals.

kinetics with respect to DBCP (Table 4). With pelleted Pd/ γ -Al₂O₃, however, DBCP removal followed zero-order kinetics (discussed below). Pd/ γ -Al₂O₃ powder obtained from different manufacturers (Alfa or Aldrich) yielded similar reactivities with an average k_{obs} of $0.22 \pm 0.03 \text{ min}^{-1}$. Reaction rates depended upon the type and morphology of the catalyst support, with rates increasing in the following order:

PEI/SiO₂ beads < activated C powder

< PEI/SiO₂ powder < γ -Al₂O₃ powder.

Similar experiments using powdered γ -Al₂O₃, C and beaded PEI/SiO₂ but with PCE as a substrate (Schreier and Reinhard, 1995) are included in Table 4 for comparison. Hydrodehalogenation using powdered Pd/ γ -Al₂O₃ was most rapid regardless of substrate. The transformation rates using powdered Pd/ γ -Al₂O₃, Pd/C, or beaded Pd/PEI/SiO₂ were also similar for the two substrates. In addition, PCE transformation rates with various supports increased in the same order as above. Apparently, the rate of hydrodehalogenation is more dependent upon the catalyst type and morphology than the structure of the substrate, at least for the halogenated aliphatic (DBCP) and olefin (PCE) compounds investigated here.

Reactions of H₂/Pd in groundwater.

Product Distribution Studies

Figure 5 illustrates the quantitative transformation of DBCP to propane with the transient formation of propene using pelleted Pd/ γ -Al₂O₃. No halogenated intermediates were detected. The transient formation of propene is consistent with the lower pathway of Scheme 1. Propene may be formed by sequential dihaloelimination, elimination, and/or hydrogenolysis reactions. The reaction was zero-order with respect to DBCP, probably because of mass transfer limitations since only one pellet of 0.5% Pd/ γ -Al₂O₃ was used in 75 ml solution. As anticipated, increasing the number of Pd/ γ -Al₂O₃ pellets from 1 to 4 resulted in proportionately higher observed rate constants ranging from 0.36 to 0.14 $\mu\text{M}/\text{min}$ (or $0.36 \pm 0.02 \mu\text{M}/\text{min}$ per pellet). Note that pH did not

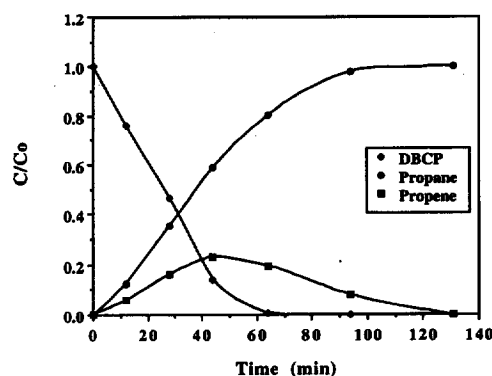


Fig. 5. Product distribution of DBCP transformation into 100% propane via propene using 45 mg of Pd/ γ -Al₂O₃ (1 pellet) in 75 ml groundwater spiked (pH 8.3) with 18 μ M DBCP at 22°C and 0.1 atm H₂ partial pressure. Line on the DBCP data was determined by linear regression. The propane and propene data did not fit simple kinetic models and the line on these data is an arbitrary polynomial fit.

noticeably increase in these systems as it did in iron experiments with groundwater.

Effect of Solution Composition

DBCP transformation by Pd in unbuffered groundwater was approximately 28% slower than transformation in unbuffered Milli-Q[™] water (compare Entry 1 in Tables 4 and 5). This relatively small difference indicates that DBCP destruction by H₂/Pd is relatively insensitive to the aqueous phase composition, at least for the groundwater studied.

The rate data summarized in Table 5 show that all ions tested (SO₄²⁻, NO₃⁻, Cl⁻, and SO₃²⁻) slowed DBCP transformation, although to significantly different degrees. For example, sulfite (27.9 mg/l) had the greatest effect, decreasing the zero-order reaction rate by nearly 90%, while SO₄²⁻, NO₃⁻, and Cl⁻ decreased the rate by $\leq 50\%$. The mechanism of catalyst deactivation by sulfite was probably reduction of sulfite to bisulfide, HS⁻ (HS⁻ is known to poison Pd catalysts toward hydrodehalogenation of PCE (Schreier and Reinhard, 1995)), but this hypothesis was not tested.

DBCP transformation in O₂-saturated (41.6 mg/l) groundwater was about 60% slower than in the anoxic case ($k_{\text{obs}}^0 = 0.40 \pm 0.01 \text{ nM}/\text{min}$ for O₂-saturated; $k_{\text{obs}}^0 = 1.01 \pm 0.07 \text{ nM}/\text{min}$ for anoxic). Thus,

Table 5. Effect of dissolved ions on the zero-order rate constants of DBCP transformation using 45 mg of Pd/ γ -Al₂O₃ (1 pellet) in 75 ml unbuffered groundwater spiked with 18 μ M DBCP at 22°C and 0.1 atm H₂ partial pressure

System	$k_{\text{obs}}^0 (\mu\text{M}/\text{min})^a$	Relative removal rates
No ions (0 mg/l)	0.36 ± 0.02	1.00
SO ₄ ²⁻ (28.0 mg/l)	0.22 ± 0.02	0.61
NO ₃ ⁻ (28.2 mg/l)	0.19 ± 0.01	0.53
Cl ⁻ (100.3 mg/l)	0.17 ± 0.02	0.47
SO ₃ ²⁻ (27.9 mg/l)	0.038 ± 0.001	0.11

^aErrors are 95% confidence intervals.

under typical water treatment conditions (0–10 mg/l O_2), some inhibition may occur, but not to a significant extent.

SUMMARY AND CONCLUSIONS

Both Fe^0 powder and H_2/Pd catalyst hydrodehalogenate DBCP quantitatively to propane in water under water treatment conditions (pH 7.0–8.7 and 22°C). In both cases, propene was the only intermediate detected. Reductive dehalogenation of DBCP by Fe^0 appeared to be sensitive to pH and groundwater composition. Rapid transformation with Fe^0 was dependent upon the presence of HEPES buffer in both Milli-Q[™] water and groundwater; for example, the reaction rate in unbuffered groundwater was about seven times slower than in HEPES-buffered groundwater. The reaction rate in groundwater also depended upon the type of buffer or acid used to adjust the pH. Specifically, HCl or HNO_3 reduced the reaction rate despite lowering the pH from above 8 to 7, while lowering the pH with H_2SO_4 , $HClO_4$ or acetic acid enhanced the rates slightly. Dissolved O_2 and NO_3^- caused a minor decrease in the rate, while NO_2^- and SO_4^{2-} had little or no effect. Fe^0 was initially inactive unless it was first exposed to H_2 atmosphere (10% in N_2). It is not clear whether activation of the metal was due to simple displacement of adsorbed oxygen or due to dissociative adsorption of H_2 .

Fe^0 contacting may serve as a method for removing low concentrations of NO_3^- (≤ 60 mg/l) from water since the reaction is fast at room temperature and neutral pH. In all cases, nitrate was reduced by Fe^0 to nitrite which was also completely removed by Fe^0 . It has long been known that nitrate was reducible by Fe^0 during the corrosion cracking processes of steels in nitrate solutions, but to the best of our knowledge, the potential application of Fe^0 to treat nitrate and/or nitrite-contaminated water has not been studied.

DBCP hydrodehalogenation in groundwater by H_2/Pd was facile and not strongly dependent on HEPES buffer. Specifically, the transformation rate in unbuffered groundwater using pelleted $Pd/\gamma-Al_2O_3$ was about the same as in Milli-Q[™] water suggesting that hydrodehalogenation using Pd catalyst is less sensitive to pH and groundwater composition than reductive dehalogenation using Fe^0 . SO_4^{2-} , NO_3^- , and Cl^- decreased the DBCP transformation rate by up to about 50%. SO_3^{2-} decreased the rate significantly (by 90%) perhaps due to the formation of HS^- which is known to poison the catalyst.

Zero-valent iron reductive dehalogenation is potentially a useful *in situ* method, while Pd-catalyzed hydrodehalogenation is potentially a viable above-ground technique for the treatment of groundwater contaminated with DBCP. The potential risks of using hydrogen in large-scale treatment facilities utilizing the H_2/Pd process will have to be addressed by considering industrial safety standards for H_2 use.

However, more studies are needed to reliably extrapolate these data to large-scale treatment systems and to compare the treatment costs with that of alternative technologies.

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